Reduced Molybdovanadophosphates[‡]

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The equilibrium speciation in the aqueous $H^+/MoO_4^{2-}/HVO_4^{2-}/HPO_4^{2-}/e^-$ system, 0.600 M Na(Cl) medium at 25 °C, was characterised by potentiometric $[H^+]$ (glass electrode) and $\{e^-\}$ (platinum electrode) titration techniques as fundamental tools, complemented by $^{51}V^V$ NMR (131.6 MHz) and V^{IV} ESR spectroscopy. The study has been focused on solutions with the Keggin ratio, (Mo + V)/P = 12:1 and Mo/V > 5, in the pH range 1.4–4.5, where anions having the formula $[H_zMo_{12-x-y}V^V_xV^{IV}_yPO_{40}]^{(3+x+2y-z)-}$ are predominant species. Added numbers of electrons per vanadium(V) (e^-/V^V) have been kept less than one to exclude reduction of molybdenum(VI). Six reduced molybdovanadophosphate species have been identified. The $[Mo_{11}V^{IV}PO_{40}]^{5-}$ species [$\log\beta = 154.15 \pm 0.03$ (3σ)] and the mixed-valence species $[Mo_{10}V^VV^{IV}PO_{40}]^{6-}$ ($\log\beta = 155.84 \pm 0.02$) can both be monoprotonated. These species have pK_a values of 0.93 and 3.68, respectively. A "fully" reduced Keggin species, $[H_2Mo_{10}V^{IV}{}_2PO_{40}]^{5-}$ ($\log\beta = 171.27 \pm 0.06$), and a lacunary $[H_4Mo_{10}V^{IV}PO_{39}]^{5-}$ species ($\log\beta = 142.0 \pm 0.2$) were found as well. Except for the molybdovanadophosphate species, the only reduced species formed, in the present investigation, is the vanadyl ion, VO^{2+}. $\log K_{red}$ ($2\ H^+ + VO_2^+ + e \rightleftarrows VO^{2+} + H_2O$) was determined to 17.15 ± 0.01 ($E^0 = 1014.5 \pm 0.6$ mV).

Introduction

Polyoxoanions are of considerable interest as redox catalysts, for they are easily reduced and can often be reoxidised by O_2. Molybdovanadophosphate complexes have for example been used as catalysts in the selective oxidation of olefins to carbonyl groups.[1] Studies of solutions containing vanadium(IV), tungsten, and phosphorus[2−7] or vanadium(IV), molybdenum, and phosphorus[3,8−12] are frequently reported in the literature. In both cases so-called mixed addenda Keggin species are formed. In most of these studies the experimental techniques used have been cyclic voltammetry, NMR, and ESR. Recently, results from investigations of solutions containing vanadium(IV), tungsten, molybdenum, and phosphorus, forming Keggin anions with three addenda atoms, have been reported.[13,14]

As a part of our studies of the equilibrium speciation in the aqueous molybdovanadophosphate system, the electron has been included as the fifth component. A complete study of this system can only be done when all the oxidised and reduced subsystems are known at the same experimental conditions. The oxidised subsystems are the three binary systems H^+/MoO_4^{2-},[15] H^+/HVO_4^{2-},[16−18] and H^+/HPO_4^{2-},[19] the three ternary systems $H^+/MoO_4^{2-}/HVO_4^{2-}$,[20,21] $H^+/MoO_4^{2-}/HPO_4^{2-}$,[22,23] and $H^+/HVO_4^{2-}/HPO_4^{2-}$,[19] and the quaternary system $H^+/MoO_4^{2-}/HVO_4^{2-}/HPO_4^{2-}$.[24,25] Within the concentration ranges of this study, it was found that the only reduced species, except for those with five components, was the vanadyl cation, VO^{2+}. The formation constant for VO^{2+} has already been determined,[17] but is redetermined here with more advanced equipment.

The present system has, like all the subsystems, been studied in 0.600 M Na(Cl) medium at 25 °C. Species and formation constants have been determined by using potentiometric $[H^+]$ (glass electrode) and $\{e^-\}$ (platinum electrode) titration techniques as fundamental tools, complemented by NMR and ESR spectroscopy. One prerequisite of working with complicated systems is to have access to a computer program, which can treat all kinds of data simultaneously. Therefore, all calculations for determining the formation constants were made with the calculation program LAKE,[26] which can treat both potentiometric (EMF) and NMR spectroscopic data simultaneously.

Notations and Designations

The formation constants are reported with H^+, MoO_4^{2-}, HVO_4^{2-}, HPO_4^{2-}, and e^- as components. The equilibria are written according to Equation (1).

[‡] Multicomponent Polyanions, 50. − Part 49: Ref.[25]

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$$p\,H^+ + q\,MoO_4^{2-} + r\,HVO_4^{2-} + s\,HPO_4^{2-} + t\,e^- \rightleftarrows [(H^+)_p(MoO_4^{2-})_q(HVO_4^{2-})_r(HPO_4^{2-})_s(e^-)_t]^{p-2(q+r+s)-t} \quad (1)$$

A species formed will, for brevity, sometimes be denoted by its (*p*,*q*,*r*,*s*,*t*) integers. The potentiometric data can only establish the composition and charge of the species formed, as water may be gained or lost relative to the components. However, when complementary structural information is available, the formula can be given. For example, since in the present study (23,11,1,1,1) is known to have the Keggin composition it can be written $[HMo_{11}V^{IV}PO_{40}]^{4-}$. The charge and number of oxygen atoms and protons are often omitted below, and species are instead written in the compact forms $Mo_{11}VP$ and $Mo_{10}V_2P$. Our definition of the degree of reduction, denoted z_e, is equivalents of electrons added per mol of vanadium(V). Thus, a z_e value of 0.25, means that 25% of the vanadium, initially of valence V, is reduced.

A 0.600 M Na(Cl) ionic medium is 0.600 M Na^+ with Cl^- providing counteranion balance not provided by the oxometalate anions. The acidity measurements are on the concentration scale, where $pH = -\log[H^+]$, and *not* on the activity scale, $pH = -\log\{a_{H+}\}$. For brevity, the total concentrations of molybdenum, vanadium, and phosphorus will be denoted Mo, V, and P.

Results and Discussion

To fully understand the reduced molybdovanadophosphate system, all subsystems, both oxidised and reduced, must be known at the same experimental conditions. All oxidised subsystems have already been determined and the only reduced non-Keggin vanadium species present in this study is VO^{2+}. It is formed when the $H_zMo_{12-x-y}V^V_xV^{IV}_yP$ species decompose in acidic solutions. In the decamolybdodivanadophosphate system it was found that the ^{51}V NMR signal disappears as soon as one electron is added to the complex. One would expect that the vanadium atom, well separated from the reduced vanadium atom, should not be affected, but due to an electron tunnelling effect even this signal disappears. Similar observations have been made in studies on the reduced molybdotungstohosphate system showing that tungsten atoms, not adjacent to the reduced molybdenum atom, are affected of the reduction.[27,28]

The Reduced Vanadate System

The $H^+/HVO_4^{2-}/e^-$ system had been studied earlier in acidic solutions and in the same medium [0.600 M Na(Cl)], but with rather simple equipment.[17] Therefore, a redetermination using more advanced equipment and a more sophisticated technique for working with air-sensitive solutions was found worthwhile. Since VO^{2+} is the only reduced non-Keggin vanadium species present, only one reaction and one equilibrium constant ($\log K_{red}$) has to be determined; $2\,H^+ + VO_2^+ + e^- \rightleftarrows VO^{2+} + H_2O$, $\log K_{red} = 17.15 \pm 0.01$ ($E^0 = 1014.5 \pm 0.6$ mV), can be compared with the old result of 17.37. When the redox equilibrium is written with the components used in the study of the five component system, $5\,H^+ + HVO_4^{2-} + e^- \rightleftarrows VO^{2+} + 3\,H_2O$, the $\log\beta_{5,0,1,0,1}$ value is 32.03 ± 0.01. NMR and ESR spectra were recorded to establish that VO_2^+ and VO^{2+} are the only species formed in acidic solutions (pH < 2). ESR spectra of VO^{2+} reveal a typical vanadium(IV) signal, with 8 hyperfine lines arising from the unpaired electron ($S = 1/2$) with the nuclear spin ($I = 7/2$). ESR and NMR spectra recorded on the same solutions showed the 8-line ESR pattern for VO^{2+} increasing in proportion to the decrease of the VO_2^+ resonance in the NMR spectrum.

The Reduced Molybdovanadophosphate System

In the determination of formation constants of reduced molybdovanadophosphate species, both EMF and ^{51}V integral data were included. Calculations have been made stepwise by gradually decreasing the Mo/V ratio and expanding the pH range. Starting with different rather high Mo/V ratios (11−22), where only $Mo_{11}VP$ species and some MoP species are present, constants for the reduced $Mo_{11}V^{IV}P$ species could be determined. Once these constants were known, data from lower Mo/V ratios, down to 5.67, where also $Mo_{10}V_2P$ species are present in oxidised solutions, were included in the calculations. Different formulations for reduced species were systematically tested using LAKE. Table 1 shows the model that gave the best (lowest sum of squared errors) fit of data. Of the reduced species found, $[Mo_{11}V^{IV}PO_{40}]^{5-}$ can be monoprotonated ($pK_a = 0.93$), in contrast to the oxidised $[Mo_{11}V^VPO_{40}]^{4-}$ species.[25] The $Mo_{10}V_2P$ species with mixed valence states of vanadium, $Mo_{10}V^VV^{IV}P$, can also be monoprotonated, having a pK_a value of 3.68. A diprotonated doubly reduced species, $[H_2Mo_{10}V^{IV}_2PO_{40}]^{5-}$, is also found. An X-ray structure study on deep blue tabular crystals obtained when concentrating a fully reduced molybdovanadophosphate solution (Mo/V = 5.67; pH ≈ 4.8; $z_e = 1.0$), showed that the doubly reduced species have an α-Keggin structure.[29] One incomplete Keggin species, (20,10,1,1,1), an $Mo_{10}V^{IV}P$ species, is required in the model to explain data. Incomplete Keggin species (often called lacunary species e.g. with tungsten and Si,[30] B,[31] or P[32] as heteroatoms) are well known

Table 1. The equilibrium model obtained from calculations on data in the pH range 1.4 < pH < 4.5 and at Mo/V>5

(*p*,*q*,*r*,*s*,*t*)	Formula	logβ ± 3σ	p*K*a
22,11,1,1,1	$[Mo_{11}V^{IV}PO_{40}]^{5-}$	154.15 ± 0.03	
23,11,1,1,1	$[HMo_{11}V^{IV}PO_{40}]^{4-}$	155.08 ± 0.15	0.93
21,10,2,1,1	$[Mo_{10}V^VV^{IV}PO_{40}]^{6-}$	155.84 ± 0.02	
22,10,2,1,1	$[HMo_{10}V^VV^{IV}PO_{40}]^{5-}$	159.52 ± 0.04	3.68
23,10,2,1,2	$[H_2Mo_{10}V^{IV}_2PO_{40}]^{5-}$	171.27 ± 0.06	
20,10,1,1,1	$[H_4Mo_{10}V^{IV}PO_{39}]^{5-}$	142.04 ± 0.20	

in heteropoly anion systems. Such a lacunary species of a generalised polyhedral structure is shown in Figure 1. Accordingly, (20,10,1,1,1) most probably has the lacunary Keggin formula $[H_4Mo_{10}V^{IV}PO_{39}]^{5-}$. This lacunary species is most likely formed by dissociation of VO^{2+} from the double reduced divanadium Keggin species.

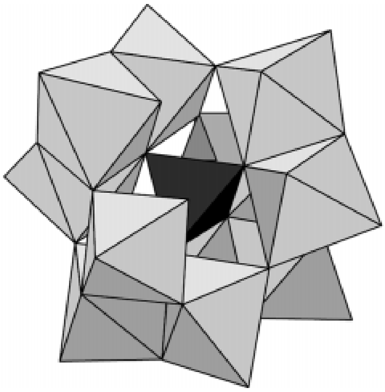

Figure 1. Polyhedral structure of an incomplete Keggin anion, a so-called lacunary species

Figure 2 shows distribution diagrams of a) vanadium and b) phosphorus for a solution where 50% of the vanadium(V) atoms are reduced to vanadium(IV). The fully oxidised solution had a composition of 20% $Mo_{11}VP$ and 80% $Mo_{10}V_2P$. The $(\alpha_i)_{V(P)}$ coordinate quantitates the fraction of every species i relative to the total V(P). Each species has its own region in the cumulative diagram, so that the fraction of the species is the region's vertical extent, at a given pH. A bold line separates reduced and oxidised species. In this figure, each protonation step is plotted individually with a dotted line and the solid line shows the sum of them. The symbols (O) in Figure 2 (a) represent experimental points (integral values) and show how the experimental NMR spectroscopic data fit the proposed model. The fit is within the evaluation error of the integrals.

In acidic solutions (pH < 2.5) there is considerable decomposition of reduced $Mo_{10}V_2P$ species to VO^{2+} and $Mo_{11}V^{IV}P$ species. Where VO^{2+} is the predominant reduced species, most of the phosphorus atoms are bound in oxidised species or present as phosphoric acid.

Comparison between Distribution Diagrams and NMR Spectra

^{51}V NMR spectra of acidic solutions (pH ≈ 2) containing 20% $Mo_{11}VP$ and 80% $Mo_{10}V_2P$ at different z_e values have been recorded on an absolute intensity mode, as shown in Figure 3. At this rather low pH value, the resonance arising from $Mo_{11}VP$ (a) decreases first when electrons are added, cf. spectra at $z_e = 0$ and 0.10. When almost all of the $Mo_{11}VP$ species has been reduced, the positional isomers of the $Mo_{10}V_2P$ (b−e) species start to reduce. In more acidic solutions (pH ≈ 1.5) the behaviour is different, the $Mo_{10}V_2P$ isomers are the first to be reduced. The redox reactions are thus very dependent upon the pH of the solutions. The simplified distribution diagram in Figure 4 shows the difference between the oxidised $Mo_{11}VP$ and $Mo_{10}V_2P$ species in solutions with $z_e = 0.0$ (full-drawn lines) and $z_e = 0.10$ (dashed lines). The $Mo_{11}VP$ species is present with approximately the same amount in oxidised and reduced solutions at pH ≈ 1.5, while it is almost completely reduced at pH ≈ 2.1. This was also experimentally observed in the NMR spectra recorded from such solutions.

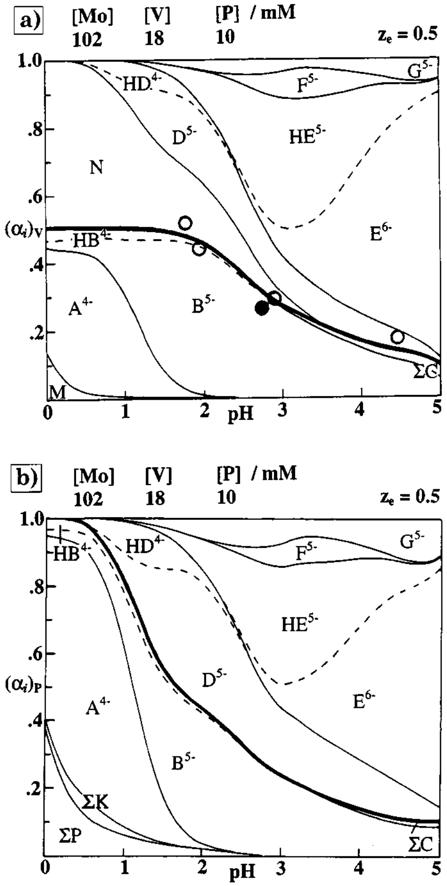

Figure 2. Distribution diagrams of a) vanadium and b) phosphorus at $z_e = 0.5$ and (Mo + V)/P = (102 + 18)/10 mM; oxidised and reduced species are separated with a bold line; each protonation step is plotted individually with a dotted line and the solid line shows the sum of them; symbols (O) represent ^{51}V integral data, and (●) is the integral value from the equilibrated, "aged", solution in Figure 5; $A^{4-} = Mo_{11}VP^{4-}$; $B^{5-} = Mo_{10}V_2P^{5-}$; $HB^{4-} = HMo_{10}V_2P^{4-}$; $\Sigma C = \Sigma Mo_9V_3P$; $M = VO_2^+$; $D^{5-} = Mo_{11}V^{IV}P^{5-}$; $HD^{4-} = HMo_{11}V^{IV}P^{4-}$; $E^{6-} = Mo_{10}V^VV^{IV}P^{6-}$; $HE^{5-} = HMo_{10}V^VV^{IV}P^{5-}$; $F^{5-} = H_2Mo_{10}V^{IV}{}_2P^{5-}$; $G^{5-} = H_4Mo_{10}V^{IV}P^{5-}$; $N = VO^{2+}$; $\Sigma P = \Sigma H_3PO_4$; $\Sigma K = \Sigma Mo_xP_y$

To examine which one of the five positional $Mo_{10}V_2P$ isomers[24] is the first to be reduced, a ^{51}V NMR spectrum was recorded immediately after the electrons had been added from a potentiostat to $z_e = 0.50$ (fresh) and then at equilibrium 2 d later (aged), Figure 5. A comparison between the two spectra shows that the resonance from the α-1,4-$Mo_{10}V_2P$ isomer (b), where two vanadium octahedra share edges, decreases more than the others in fresh solution; but after equilibrium, the ratio between all the isomers

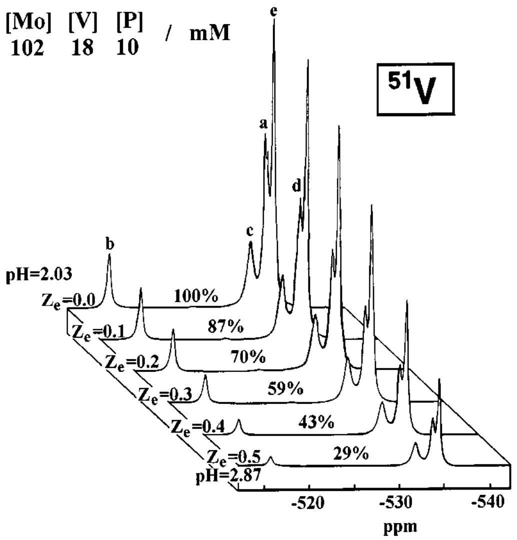

Figure 3. A set of ^{51}V NMR spectra of a solution containing 80% $Mo_{10}V_2P$ and 20% $Mo_{11}VP$ at different degrees of reduction recorded on an absolute intensity mode; resonance labelled **a** arise from the $Mo_{11}VP$ species and resonances **b**−**e** from the $Mo_{10}V_2P$ isomers; **b** = α-1,4; **c** = α-1,2; **d** = α-1,5; **e** = α-1,6 + α-1,11

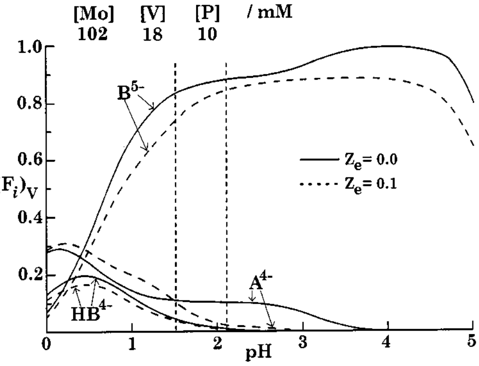

Figure 4. A simplified distribution diagram for a solution with (Mo + V)/P = (102 + 18)/10 mM, where only some oxidised species are shown at two different z_e values; full-drawn lines represent the distribution at z_e = 0.0 and dashed lines at z_e = 0.1; A^{4-} = $Mo_{11}VP^{4-}$; B^{5-} = $Mo_{10}V_2P^{5-}$; HB^{4-} = $HMo_{10}V_2P^{4-}$

are the same as in a fully oxidised solution. This means that the α-1,4-$Mo_{10}V_2P$ isomer (b) takes care of most of the added electrons in the start, but at equilibrium all isomers have the same amount of reduction. In non-aqueous solutions, a similar reduction pattern has been observed. The isomers with vicinal vanadium atoms seem to be the first to be reduced.[33] The distribution diagram in Figure 2 (a) shows that an equilibrated solution at z_e = 0.5 and pH = 2.75, should have 71% of the total vanadium in fully or partially reduced species. Experimentally, the equilibrated solution in Figure 5 has an integral value showing that 27% of the total vanadium is present in nonreduced species [marked with ● in Figure 2 (a)].

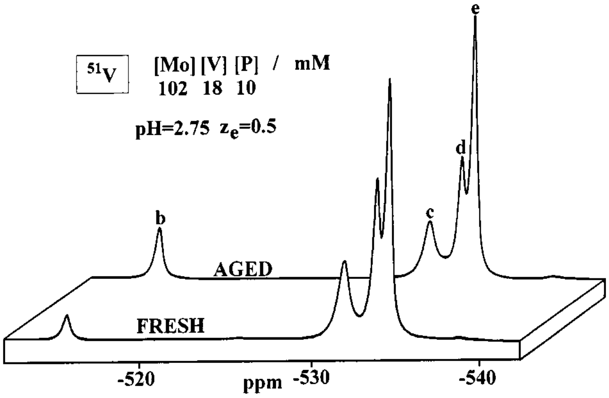

Figure 5. Two ^{51}V spectra recorded on the same $Mo_{10}V_2P$ solution; the front spectrum was recorded only a few minutes after the electrons were added with a potentiostat, and the rear spectrum after equilibration; resonances arising from the $Mo_{10}V_2P$ isomers are labelled **b**−**e**; **b** = α-1,4; **c** = α-1,2; **d** = α-1,5; **e** = α-1,6 + α-1,11

Comparison between Distribution Diagrams and ESR Spectra

In a solution with pH ≈ 2, containing both $Mo_{11}VP$ and $Mo_{10}V_2P$ species, the first species to be reduced when electrons are added is $Mo_{11}VP$, since its resonance disappears first, cf. Figure 3. A distribution diagram of a solution, where 10% of the total amount of vanadium is reduced is shown in Figure 6 (a). At pH = 2.1 the only reduced species is $[Mo_{11}V^{IV}PO_{40}]^{5-}$. An ESR spectrum [Figure 6 (b)] of the same solution indeed corresponds to the feature of $[Mo_{11}V^{IV}PO_{40}]^{5-}$ alone. The ESR spectrum of a solution with the ratio (Mo + V)/P = (110 + 10)/10 mM, reduced to z_e = 1.0 at pH = 1.0 is shown in Figure 7 (a). From our model, three reduced species should be present in such a solution, 42% $[Mo_{11}V^{IV}PO_{40}]^{5-}$, 40% $[HMo_{11}V^{IV}PO_{40}]^{4-}$, and 18% $[V^{IV}O]^{2+}$ [Figure 7 (b)]. Arrows in Figure 7 (a) mark peaks arising from VO^{2+}. Subtracting VO^{2+} from this spectrum gives the same pattern as in Figure 6 (b), which means that both the protonated and deprotonated $Mo_{11}V^{IV}P$ have the same ESR spectrum. Similar checks of the proposed model against ESR spectra were also made at different pH values and different Mo/V ratios and the agreement was good.

ESR spectra of the present system should be virtually the same as for the corresponding vanadotungstates, reported by Pope et al.[2] Five positional isomers of $W_{10}V_2P$ and $Mo_{10}V_2P$ occur in both systems. Two isomers have neighbouring vanadium atoms and in the remaining three isomers one or more tungsten/molybdenum atoms separate the two vanadium atoms. The relative statistical abundances are 12 + 12 = 24 and 12 + 24 + 6 = 42, respectively. These have been verified in solution by ^{31}P NMR for both $W_{10}V_2P$[2] and $Mo_{10}V_2P$.[24] The unpaired electron in the

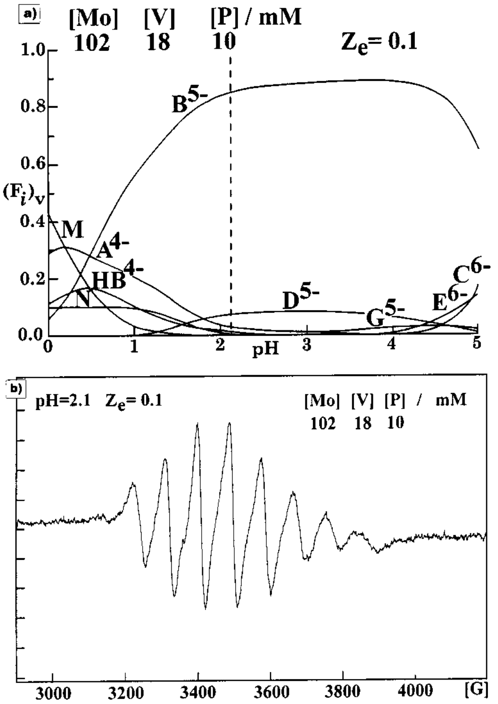

Figure 6. a) Distribution diagram of vanadium at $z_e = 0.1$ and (Mo + V)/P = (102 + 18)/10 mM; A^{4-} = $Mo_{11}VP^{4-}$; B^{5-} = $Mo_{10}V_2P^{5-}$; HB^{4-} = $HMo_{10}V_2P^{4-}$; C^{6-} = $Mo_9V_3P^{6-}$; M = VO_2^+; D^{5-} = $Mo_{11}V^{IV}P^{5-}$; E^{6-} = $Mo_{10}V^VV^{IV}P^{6-}$; G^{5-} = $H_4Mo_{10}V^{IV}P^{5-}$; N = VO^{2+}; b) ESR spectrum of the solution marked with a dashed line in a), showing the 8-line feature for $[Mo_{11}V^{IV}PO_{40}]^{5-}$

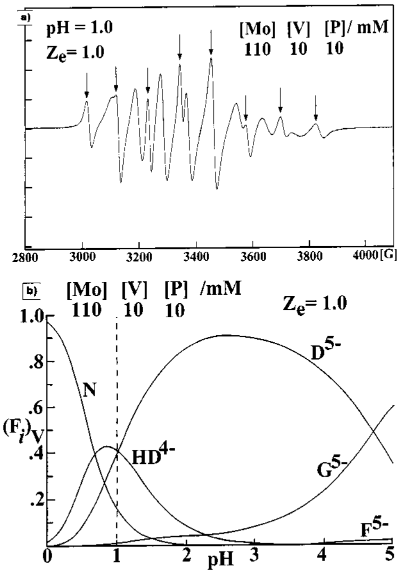

Figure 7. a) ESR spectrum of a solution with (Mo + V)/P = (110 + 10)/10 mM reduced to $z_e = 1.0$; arrows mark peaks arising from VO^{2+}; b) distribution diagram of vanadium for the same concentrations; dashed line marks the solution recorded on ESR in a); D^{5-} = $Mo_{11}V^{IV}P^{5-}$; HD^{4-} = $HMo_{11}V^{IV}P^{4-}$; F^{5-} = $H_2Mo_{10}V^{IV}{}_2P^{5-}$; G^{5-} = $H_4Mo_{10}V^{IV}P^{5-}$; N = VO^{2+}

two isomers with vicinal vanadium atoms, interacts with both vanadium nuclei through rapid intramolecular hopping to give a 15-line spectrum. In the remaining three isomers, where vanadium atoms are separated, the electron is effectively trapped by a single vanadium atom, thus giving an 8-line spectrum.[2] The relative intensity of the overlapping 15- and 8-line spectra in a mixed-valence vanadium solution should be 24:42 = 4:7. From our model, a solution with the ratio Mo/V = 102:18 = 5.7 and pH = 4.5 contains predominantly $Mo_{10}V^VV^{IV}P$ when $z_e = 0.5$. As expected, an ESR spectrum of the $Mo_{10}V^VV^{IV}P$ solution (Figure 8, bottom spectrum) shows a mixed 8- and 15-line pattern. The 8-line feature in the figure has, however, higher intensity than the 15-line, which means that the abundance observed by ESR is in accordance with the statistical prediction. In contrast, the doubly reduced $W_{10}V_2P$ species gives a spectrum with 15 equal lines, expected for the interaction of the unpaired electrons with two vanadium nuclei.[2] In the present work, a solution with the ratio Mo/V = 200:40 = 5 and pH = 4.5, which should contain 50% $Mo_{10}V^VV^{IV}P$ and 50% $Mo_{10}V^{IV}{}_2P$ species when $z_e = 0.75$, gave rise to the top 15-line spectrum shown in Figure 8. It has both the previous (8 + 15)-line component feature arising from $Mo_{10}V^VV^{IV}P$ species and also a 15-line component feature from $Mo_{10}V^{IV}{}_2P$ species, with an increase for the latter compared with the lower spectrum in Figure 8. This shows again that the proposed model is in good agreement with the experimental data.

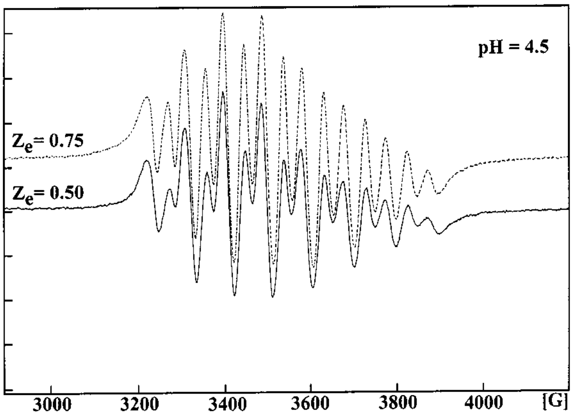

Figure 8. The bottom spectrum ($z_e = 0.5$) shows the (8 + 15)-line feature for the mixed valence state of the $Mo_{10}V^VV^{IV}P$ isomers; the top dashed spectrum ($z_e = 0.75$) shows how the 15-line pattern has increased when $Mo_{10}V^{IV}{}_2P$ also is present in the solution

Pourbaix Diagrams

The redox speciation in systems with few components is often illustrated in the literature by means of predominance diagrams, so-called Pourbaix diagrams [showing areas of predominant species as a function of *E* (or *p*e) and pH]. Numerous diagrams are needed to illustrate the speciation in the present 5-component system. The reason is that the speciation is not only dependent on the total concentrations, but also on the Mo/V/P ratios. Figure 9 shows a diagram of vanadium containing species at (Mo + V)/P = (105 + 15)/10 mM (equal amounts of $Mo_{11}VP$ and $Mo_{10}V_2P$). At high *E* values (oxidised solutions), $Mo_{11}VP$ is the predominant species at the pH range 0.2−1.3. In less acidic solutions at this high E value, the deprotonated $Mo_{10}V_2P$ isomers are predominant. When the E value is lowered, i.e. electrons have been added, these species are reduced to VO^{2+} and the monoprotonated $Mo_{11}V^{IV}P$, respectively. As can be seen from the figure, additional reduced species appear as predominant species at pH values higher than 3.4.

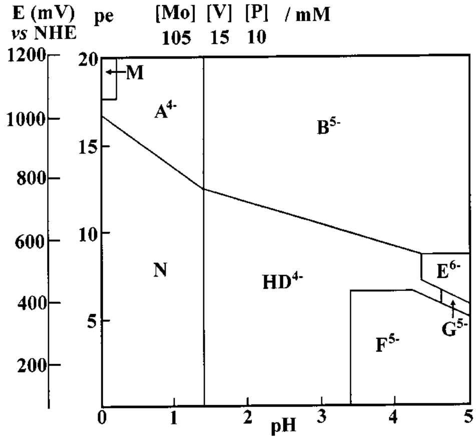

Figure 9. Predominance (Pourbaix) diagram of vanadium at (Mo + V)/P = (105 + 15)/10 mM; A^{4-} = $Mo_{11}VP^{4-}$; B^{5-} = $Mo_{10}V_2P^{5-}$; M = VO_2^+; HD^{4-} = $HMo_{11}V^{IV}P^{4-}$; E^{6-} = $Mo_{10}V^VV^{IV}P^{6-}$; F^{5-} = $H_2Mo_{10}V^{IV}{}_2P^{5-}$; G^{5-} = $H_4Mo_{10}V^{IV}P^{5-}$; N = VO^{2+}

Experimental Section

Solutions for Potentiometric, NMR, and ESR Studies: The oxidised solutions for potentiometric, NMR, and ESR studies were prepared as previously described.[24,25] Stock solutions of vanadium(IV) were prepared from vanadium(IV) oxide, V_2O_4 (Aldrich Chemical 99.9%), which was dried at 100 °C and then used without any further purification. V_2O_4 was dissolved in diluted hydrochloric acid and the absence of vanadium(V) as VO_2^+ was checked by ^{51}V NMR. The dissolution process is very slow, but can be speeded up in an ultrasound bath. To make sure that no reoxidation will occur, all glassware was filled with argon and all solutions bubbled with argon for at least 30−40 min before mixing.

Equilibria: Equilibria in the reduced molybdovanadophosphate system were attained within 2−48 h, and in the reduced vanadium system within 2−24 hours. No matter how the electrons were added, coulometrically or with a vanadium(IV) stock solution, the same results were obtained. Equilibrium was, however, reached more rapidly using a vanadium(IV) solution. The redox reactions of Keggin species were shown to be reversible.

EMF Measurements: EMF titrations were conducted at 25.0 ± 0.1 °C using an automated potentiometric titrator. Free H^+ concentrations were determined by measuring the EMF of the following cell, using an Ingold type 201-NS glass electrode, an Ag/AgCl reference electrode, prepared according to Brown,[34] and a Wilhelm bridge.[35]

− Ag, AgCl | 0.600 M NaCl || equilibrium solution | measuring electrode +

The redox potential was measured between a small foil or spiral of platinum metal in the solution and the same reference electrode as for the measurements of free [H^+]. The free H^+ concentration and the electron activity were calculated from the measured EMF values E [mV] by Equation (2) and Equation (3), where the last term is the liquid junction potential for 0.6 M NaCl medium and the type of bridge used.

$$E = E_{0a} + 59.157\cdot\log[H^+] - 76\cdot[H^+] \qquad (2)$$

$$E = E_{0b} - 59.157\cdot\log\{e^-\} - 76\cdot[H^+] \qquad (3)$$

The electrons were added coulometrically at 800−250 mV vs. NHE using an automated potentiostat (developed at our department), or with a solution containing vanadium(IV) of known concentration. All titrations were performed under pure argon to prevent contamination by oxygen from the air. The argon was sparged through 10% NaOH solution to remove any acid impurities, 10% H_2SO_4 solution to remove any alkaline impurities, and, finally, 0.6 M NaCl medium before introduction to the titration vessel. Before each titration, the platinum electrode was rinsed in distilled water and heated in an ethanol flame. The constant E_{0a} was determined before and after each titration, using a separate solution of known [H^+]. In separate experiments, E_{0b} was determined to −250 mV in solutions with known {e^-}. Several experiments were performed and the variation in E_{0b} was negligible. The value −250 mV could thus be used for all titrations. Reduction constants are often reported with E^0 instead of $\log K_{red}$ values. The relation between them is described in Equation (4), where $g = (R\cdot T\cdot\ln 10)/F$ and n_e is the number of electrons in the redox reaction; at 25 °C, g = 59.157 mV.

$$E^0 = g/n_e\cdot\log K_{red} \qquad (4)$$

EMF Data: In the determination of the formation constant of the vanadyl cation, VO^{2+}, 118 data points were collected from 12 different titrations in the concentration ranges $1.5 < pH < 2.1$ and $4 < [V] < 10$ mM. To ensure that no other species than the vanadyl ion was formed, the upper limit of the z_e value was 0.92. In the reduced molybdovanadophosphate system 44 titrations were performed on Keggin ratio solutions, (Mo + V)/P = 12, with $5 < Mo/V < 22$ and $10 < Mo/P < 11$. The concentration ranges $1.38 < pH < 5.49$, $100 < [Mo] < 200$ mM, $5 < [V] < 40$ mM, and $10 < [P] < 20$ mM have been covered. In the calculations, data were restricted to the pH and z_e ranges $1.38 < pH < 4.5$ and $0.0 < z_e < 0.9$ giving in total 322 data points. To confirm that the same result is achieved both when electrons are added to an oxidised solution and when an oxidised solution is added to a reduced, titrations were made in both directions and they coincide. Since the present study has been focused on $Mo_{11}VP$ and $Mo_{10}V_2P$ species and to avoid the formation of Mo_9V_3P species, no Mo/V ratio lower than 5 was allowed. The upper limit of z_e was set at 0.9 to avoid the reduction of molybdenum(VI).

NMR Measurements: The ^{51}V and ^{31}P NMR measurements were obtained by using a Bruker AM500 spectrometer at 131.6 and 202.5 MHz, respectively. The probe temperature was thermostatted at 25.0 ± 0.5 °C. The field frequency stabilisation was locked to deuterium by placing the 8-mm sample tubes into 10-mm tubes containing D_2O. The samples were spinning in all experiments. All NMR samples were transferred from the titration solution to the sample tubes with a Hamilton® gas syringe. Commercial stainless steel needles could not be used since the steel was found to reduce oxidised MoVP solutions. Instead, specially prepared titanium needles were used. The NMR tubes used were of septa type and were "rinsed" with argon for about 45 min, to avoid oxidation of the reduced solutions by oxygen in the air. The spin-lattice relaxation time (T_1) was just a few ms for ^{51}V, so by having a relaxation delay of 1 s the spectra were quantitatively recorded. The free induction decay (FID) was multiplied by an exponential line-broadening function (LB = 1), using the Bruker software, to improve the signal/noise ratio. A Gaussian−Lorentzian double apodization was sometimes applied to the FID, also by using the Bruker software, to enhance resolution to obtain more accurate chemical shifts of overlapping resonances. $VOCl_3$ and 85% H_3PO_4 were used as external shift standards. Positive chemical shifts (δ) correspond to higher frequency. For an exact shift scale, a solution of α-$[Mo_{11}VPO_{40}]^{4-}$ = 10 mM in 0.600 M Na(Cl) medium was used as external ^{51}V and ^{31}P chemical shift standards.[24] When studying reduced solutions, the absolute intensity (AI) mode was used and spectra recorded with exactly the same experimental parameters as for a spectrum of a fully oxidised solution with known concentration of vanadium(V) and phosphorus.

NMR Spectroscopic Data: Integral values from 42 different ^{51}V spectra in the pH range 1.51−4.42 were included in the calculations. By working in an AI mode, it was possible from the total integral value to determine how much of the total vanadium is bound in oxidised and reduced species, since species containing vanadium(IV) are NMR-silent. A set of ^{51}V NMR spectra recorded in AI mode is shown in Figure 3, and the total integral values (sum of vanadium in oxidised species) of each spectrum decreases when z_e increases. ^{31}P NMR spectroscopic data have not been included in any of the calculations. Spectra were recorded only to find out if the resonances of oxidised species decrease at the same rate as for vanadium when electrons were added. When this was shown to be the case, only ^{51}V NMR spectroscopic data were recorded, since quantitative data of high quality could be obtained in much shorter time.

ESR Measurements and Data: ESR measurements on vanadium(IV) were carried out with a Bruker ESP 300E X-band spectrometer. Aqueous samples were contained in 115 μL sealed capillary tubes, and spectra scanned from 2800 G to 4200 G. The microwave power was 5 mW. No ESR data have been included in the calculations. ESR was used to (i) obtain "fingerprints" of reduced species and (ii) verify that the proposed model fitted to experimental reduced data.

Computer Programs: Resonance intensities were computed by integration using the Bruker software. By using the least-square program LAKE,[26] mathematical analysis of combined $[H^+]$ and $\{e^-\}$ data, and ^{51}V NMR integral data was accomplished. Multimethod data can be treated simultaneously in LAKE, which considerably refines the equilibrium analysis. This is the greatest advantage of the program. Calculation and plotting of distribution and predominance diagrams were performed using the program SOLGASWATER.[36]

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